

### III.A.14 SOFC Interconnect Materials Development at PNNL

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#### Objectives

- Develop cost-effective, optimized materials for intermediate-temperature solid oxide fuel cell (SOFC) interconnect and interconnect/electrode interface applications.
- Identify and understand degradation processes in interconnects and interconnect/electrode interfaces.

#### Approach

- Screening study of conventional and newly developed alloys (chemical properties, electrical properties, mechanical properties, cost).
- Investigation of degradation of alloy interconnect materials and their interfaces under SOFC operating conditions.
- Development of improved interconnect materials (surface modification, bulk modification, cathode/interconnect contact materials).

#### Accomplishments

- Completed dual atmosphere oxidation study on selected Ni-based alloys.
- Evaluated effects of moisture on oxidation of Crofer22APU ferritic stainless steel.
- Evaluated compatibility and electrical resistance of cathode/contact paste/interconnect components.

#### Future Directions

- Evaluate dual atmosphere oxidation of alloys using simulated reformat on fuel side.
- Complete study evaluating electrical properties and chemical stability of cathode/contact paste/interconnect structures.
- Develop optimized protective oxide layers to minimize electrical resistance and Cr volatility at surfaces of alloy-based interconnects.

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#### Introduction

With the reduction in SOFC operating temperatures, low-cost, high-temperature oxidation alloys have become promising candidates to replace lanthanum chromite, a ceramic that can withstand operating temperatures in the 1000°C range. To improve the understanding of the advantages and limitations of alloy interconnects, Pacific Northwest National Laboratory (PNNL) has been engaged in

systematic screening studies to identify and evaluate potential candidate materials and to examine in detail the materials issues that must be resolved. These issues include chromia scale evaporation; scale electrical resistivity in the long term; corrosion under interconnect dual exposure conditions; and scale adherence and compatibility with the adjacent components, such as seals, electrodes and/or electrical contact layers.

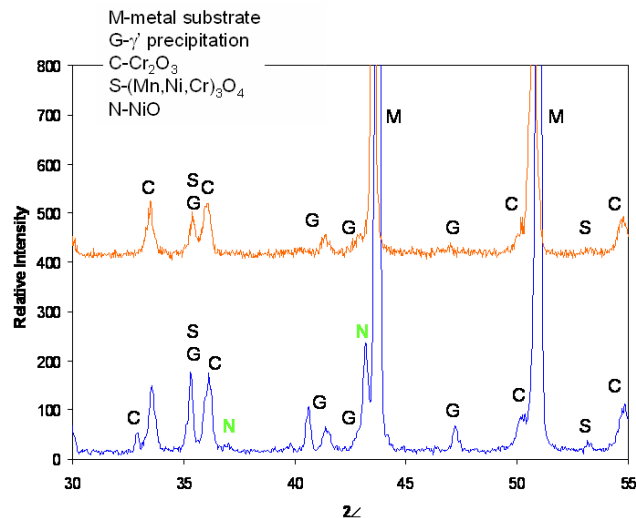
## Approach

Following earlier work on ferritic stainless steels, the oxidation behavior of nickel-based alloys was investigated under SOFC interconnect dual exposures. Specifically, the alloy samples were exposed to flowing moist air (~3% water) and moist hydrogen (also ~3% water) at 800°C in a specially designed dual atmosphere test apparatus for 300 hours. After testing, the scale morphology, chemistry, and elemental distributions were studied via x-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS), and compared with standard test samples exposed to air only at 800°C. To study the effects of water vapor in air on the oxidation behavior of Crofer22APU under single and dual exposures, a coupon was oxidized under moist hydrogen vs. moist air exposure. For alloy/cathode compatibility studies, reaction couples and electrical resistance couples were prepared and tested in air at elevated temperatures.

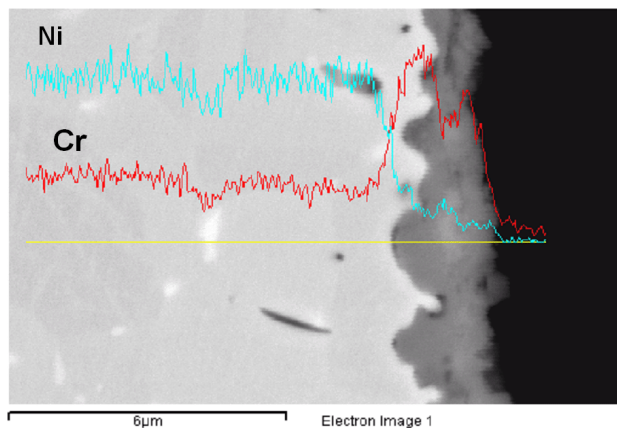
## Results

The work on oxidation behavior of selected nickel-based chromia-forming alloys (Haynes230, Hastelloy S, and Haynes242) under the hydrogen/air dual environment indicated that the dual exposure led to an oxidation behavior on the air side that differed from that observed in air only, while the oxidation behavior on the fuel side was similar to that found in fuel only. However, unlike ferritic stainless steels that often suffer localized attack at the air side via accelerated growth of iron oxide nodules, a uniform scale was observed on Hastelloy S after a duration of 300 hours at 800°C under dual exposure conditions (Figures 1 - 3). The dual atmosphere exposure produced a uniform, fine chromia-dominated scale at the air side that also contained a small amount of spinel. In comparison, the scale grown on the sample that was exposed to moist air at both sides appeared less uniform, and NiO was also observed in the scale.

Similar behavior was also observed for Haynes230 under the hydrogen/air dual environment. A uniform chromia-dominated scale grew on the air side and contained a small amount of spinel. In comparison, the scale grown on a sample



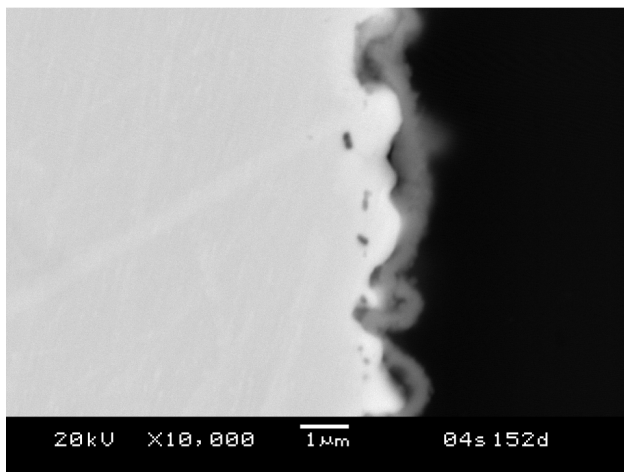
**Figure 1.** XRD Pattern of the Airside Scale Grown on Hastelloy S after Oxidization at 800°C for 300 Hours under a Moist Hydrogen/Moist Air Dual Exposure, Compared with Scale Grown in Air Only



**Figure 2.** SEM Micrograph of the Airside Scale Grown on Hastelloy S after Oxidization at 800°C for 300 Hours under a Moist Hydrogen/Moist Air Dual Exposure

that was exposed to air on both sides appeared less uniform, with occasional regions of NiO as a top layer of the scale.

For Haynes242, XRD indicated that the scale grown on the sample that was exposed to moist air at both sides was less uniform and contained more NiO than the scale grown on the air side under dual atmosphere exposure. Overall, it appears that, for



**Figure 3.** SEM Micrograph of the Airside Scale Grown on Hastelloy S after Oxidization at 800°C for 300 Hours in Moist Air Only

Ni-based superalloys with sufficient chromium, e.g. Haynes230 and Hastelloy S, dual exposure tends to facilitate the formation of a uniform chromia-dominated scale.

For Crofer22APU, a ferritic stainless steel, it was found that the scale grew homogeneously on the air side of Crofer22APU during the isothermal oxidation under moist hydrogen/air dual environment at 800°C, but contained a significant amount of iron in the top spinel layer, i.e.  $(\text{Mn,Cr,Fe})_3\text{O}_4$ . When the air (ambient, containing 1%  $\text{H}_2\text{O}$ ) was replaced by moist air (3%  $\text{H}_2\text{O}$ ) on the air side (i.e. moist hydrogen/air dual environment), the increased water partial pressure on the air side further accelerated the anomalous oxidation, resulting in nucleation and growth of hematite in the scale that led to a localized attack. In contrast, a uniform scale comprised of chromia-rich sublayer and  $(\text{Mn,Cr})_3\text{O}_4$  spinel top layer was observed on the Crofer22APU sample that was exposed to moist air at both sides.

Studies on the chemical compatibility between cathode/contact paste/interconnect components indicated that, among different perovskites, lanthanum manganite facilitates formation of a spinel layer at the contact interface which acts as a barrier to mitigate Cr migration into the perovskite. For example, after 300 hours exposure to air at 800°C, a dense, uniform  $(\text{Cr,Mn})_3\text{O}_4$  layer formed at the contact interface between a coupon of Crofer22APU

and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$  paste. EDS analysis indicated ~0.5% Cr in the manganite, which was much lower than the percentage (8-10% Cr) found in lanthanum ferrite contact pastes. The migration of Cr into the perovskite likely resulted in formation of  $\text{SrCrO}_4$ . The formation of strontium chromate was confirmed by XRD on powder mixtures of  $\text{Cr}_2\text{O}_3$  and perovskites that were heat-treated at 800°C in moist air for 300 hours.

## **Conclusions**

Under the SOFC interconnect dual exposures, the oxidation behavior of high-temperature oxidation-resistant alloys on the air side can be quite different from that observed in single atmosphere exposure. For ferritic stainless steels with a relatively low Cr percent (<23%), dual exposure enhances iron transport and in some cases leads to the formation of  $\text{Fe}_2\text{O}_3$  hematite-rich nodules in the scale. Increased water vapor in air further accelerates the anomalous oxidation behavior of ferritic stainless steel on the air side. For Ni-based alloys, the dual exposure inhibits the growth of NiO in the scale on the air side and thus facilitates the formation of uniform, protective scale. When in contact with chromia-forming alloy interconnects, manganite perovskites facilitate the formation of a  $(\text{Cr,Mn})_3\text{O}_4$  layer, which mitigates Cr migration and decreases contact resistance.

## **FY 2004 Publications**

1. Yang Z, Xia G, Singh P, Stevenson JW. "Effects of Water Vapor on the Anomalous Oxidation Behavior of Ferritic Stainless Steels under Solid Oxide Fuel Cell Operating Conditions," submitted to Acta Mater.
2. Yang Z, Xia G, Singh P, Stevenson JW. "Anomalous Oxidation Behavior of Ni Based Alloys under Solid Oxide Fuel Cell Interconnect Exposure Conditions," submitted to Scripta Mater.
3. Yang Z, Walker MS, Singh P, Stevenson JW, Norby T. "Oxidation Behavior of Ferritic Stainless Steels under Solid Oxide Fuel Cell Interconnect Exposure Conditions," *J. Electrochem Soc*, in print.

4. Yang Z, Hardy JS, Walker MS, Stevenson JW. "Structure and Electrical Conductivity of Thermally Grown Scales on Ferritic Fe-Cr-Mn Steel for SOFC Interconnect Applications," *J. Electrochem Soc*, in print.
5. Yang Z, Singh P, Stevenson JW. "Anomalous Corrosion Behavior of Stainless Steels under Solid Oxide Fuel Cell Interconnect Exposure Conditions," *Electrochem & Solid State Lett* 2003; 6:B35.
6. Yang Z, Walker MS, Singh P, Stevenson JW. "Investigation of Oxidation-Resistant Alloy Interconnects for Use in Planar SOFC," 2003 *Fuel Cell Seminar Abstracts*, Courtesy Associates, Washington, D.C. (2003).
2. Yang Z, Xia G, Singh P, Stevenson JW, "Interconnect Development," 2004 SECA Workshop, Boston, May 11-14, 2004.
3. Yang Z, Xia G, Walker MS, Singh P, Stevenson JW, "Anomalous Oxidation Behavior of Oxidation Resistant Alloys under SOFC Interconnect Dual Exposure Conditions," 133<sup>rd</sup> Annual Meeting of TMS, Charlotte, NC, March 15-17, 2004.
4. Yang Z, Xia G, Meinhardt KD, Weil KS, Singh P, Stevenson JW, "Evaluation of Crofer22 APU for SOFC Interconnect Applications," 2003 ASM Mater. Sol. Conf. & Exp., Pittsburgh, October 15-17, 2003.
5. Yang Z, Singh P, Stevenson JW, Walker MS, Xia G, "Corrosion of Ferritic Stainless Steel Interconnect under Dual Atmospheres," 2003 ASM Mater. Sol. Conf. & Exp., Pittsburgh, PA, October 15-17, 2003.

#### **FY 2004 Presentations**

1. Yang Z, Hardy JS, Paxton DM, Singh P, Stevenson JW, Walker MS, Weil KS, Xia G, "Application of High Temperature Oxidation Resistant Alloys for SOFC Interconnect Applications: Status and Challenges," 133<sup>rd</sup> Annual Meeting of TMS, Charlotte, NC, March 15-17, 2004. (Invited)